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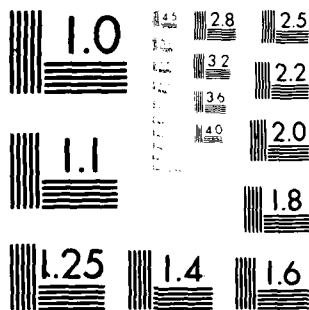
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January 1980

Report No. CNR-2-4
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RESEARCH IN ENERGETIC COMPOUNDS

By

K. Baum, T. G. Archibald, V. Grakauskas and P. T. Berkowitz

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Studies of the synthesis and polymerization of energetic oxetanes were continued. The polymerization of 3-azidooxetane, catalyzed by boron trifluoride etherate gave diols with molecular weights of 3,000 to 3,600. A gunstock was prepared with TDI. An efficient reagent for reducing 3-azidooxetane was found to be triphenylphosphine, providing a high yield of 3-aminooxetane. The reaction of 3-nitrooxetane with tetranitromethane provided an improved yield of 3,3-dinitrooxetane. The polymerization of 3,3-dinitrooxetane with phosphorus pentafluoride gave a polymer with a melting point of 200°C. Copolymers		

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20. ABSTRACT (Cont'd)

of 3,3-dinitrooxetane with 3-fluoro-3-nitrooxetane were obtained with melting points as low as 137°C.

Process development studies of 3-azidooxetane were carried out. The addition of acetic acid to epichlorohydrin was simplified by minimizing the amounts of acetic acid and ferric chloride catalyst and eliminating the use of solvent. The adduct, without work-up was treated with ethyl vinyl ether. Treatment of the product with aqueous base, followed by removal of the acetal protecting group with methanol gave 3-hydroxyoxetane. *p*-Toluenesulfonyl chloride and aqueous base gave oxetyl tosylate in 23% overall yield from epichlorohydrin. A safe procedure for reacting the tosylate with sodium azide was developed using polyethylene glycol as the reaction solvent and methylene chloride as the trapping solvent.

Studies of polynitroadamantanes were initiated. In the nitration of adamantane oximes to gem-dinitro compounds the addition of hydrogen peroxide to oxidize nitroso intermediates was found to decompose the products. 4-Bromo-2-oximinoadamantane was converted to 4-bromo-2,2-dinitroadamantane in 70% yield by reoximating and nitrating the initial product mixture containing ketone by-product. An unidentified product was obtained from 2,6-dioximinoadamantane. Halogenation of 2 oximinoadamantane gave 2-bromo-2-nitroadamantane and 2-chloro-2-nitroadamantane. Treatment of the bromo compound with sodium borohydride gave 2-nitroadamantane, and oxidative nitration gave 2,2-dinitroadamantane. The nitration of 2,6-dihydroxy-9-azabicyclo(3.3.1)nonane gave the nitramine dinitrate, which was converted to the nitramine diol.

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CONTENTS

	<u>Page</u>
I. Introduction _____	1
II. Oxetane Chemistry _____	1
A. Discussion _____	1
3-Azidooxetane Polymerization _____	1
Synthesis of 3,3-Dinitrooxetane _____	4
B. Experimental _____	7
3-Aminooxetane _____	7
3-Nitrooxetane _____	8
Reaction of 3-Aminooxetane with Peracetic Acid _____	9
3,3-Dinitrooxetane by Oxidative Nitration _____	9
3,3-Dinitrooxetane from Tetranitromethane _____	10
Polymerization of 3,3-Dinitrooxetane _____	10
Copolymer of 3,3-Dinitrooxetane and 3-Fluoro-3-nitrooxet- ane _____	11
Polymerization of 3-Azidooxetane _____	12
Gumstock Preparation _____	12
III. Process Development and Production of 3-Azidooxetane _____	13
A. Discussion _____	13
Epichlorohydrin-Acetic Acid Reaction _____	14
3-Chloro-2-(1-ethoxyethoxy)-1-propyl Acetate _____	14
3-Chloro-2-(1-ethoxyethoxy)propanol and 3-(1-Ethoxy- ethoxy)oxetane _____	15
3-Hydroxyoxetane _____	15
3-Oxetyl Tosylate _____	16

3-Azidooxetane _____	16
Other Intermediates _____	17
B. Experimental _____	17
3-Chloro-2-hydroxy-1-propyl Acetate _____	17
3-Chloro-2-(1-ethoxyethoxy)-1-propyl Acetate _____	18
3-(1-Ethoxyethoxy)oxetane _____	18
3-Hydroxyoxetane _____	19
3-Oxetyl Tosylate _____	19
3-Azidooxetane _____	19
IV. Polycyclic Nitro Compounds _____	20
A. Discussion _____	20
B. Experimental _____	25
2-Bromo-2-nitroadamantane _____	25
2-Chloro-2-nitroadamantane _____	25
2-Nitroadamantane _____	25
2,2-Dinitroadamantane _____	26
Direct Nitration of 2-Oximinoadamantane _____	26
4-Bromo-2,2-dinitroadamantane _____	27
Nitration of 2,6-Dioximinoadamantane _____	28
Reaction of 2,2-Dinitroadamantane with Hydrogen Peroxide	29
2,6-Dinitrato-9-nitro-9-azabicyclo(3.3.1)nonane _____	29
2,6-Dihydroxy-9-nitro-9-azabicyclo(3.3.1)nonane _____	31
V. References _____	32

I Introduction

This report summarizes the research under contract N00014-78-C-0147 during the period 1 January 1981 through 31 December 1981. Work was continued in the area of energetic oxetanes. Improvements were made in the synthesis routes to 3-azidooxetane and 3,3-dinitrooxetane and the latter was polymerized for the first time. Synthesis procedures for 3-azidooxetane were adapted for scale-up, and multi-pound quantities were produced. Work was initiated on the synthesis of polycyclic nitro compounds.

II Oxetane Chemistry

A. Discussion

3-Azidooxetane Polymerization. In the preceding report¹ preliminary studies of the polymerization of 3-azidooxetane were described. Of particular interest was the isolation of a difunctional polymer with a molecular weight of 2100 when the polymerization was catalyzed with boron trifluoride etherate. The polymer was a viscous oil and was stable to about 125°C. These properties, as well as a synthesis route potentially amenable to scale-up, prompted a more detailed polymer study.

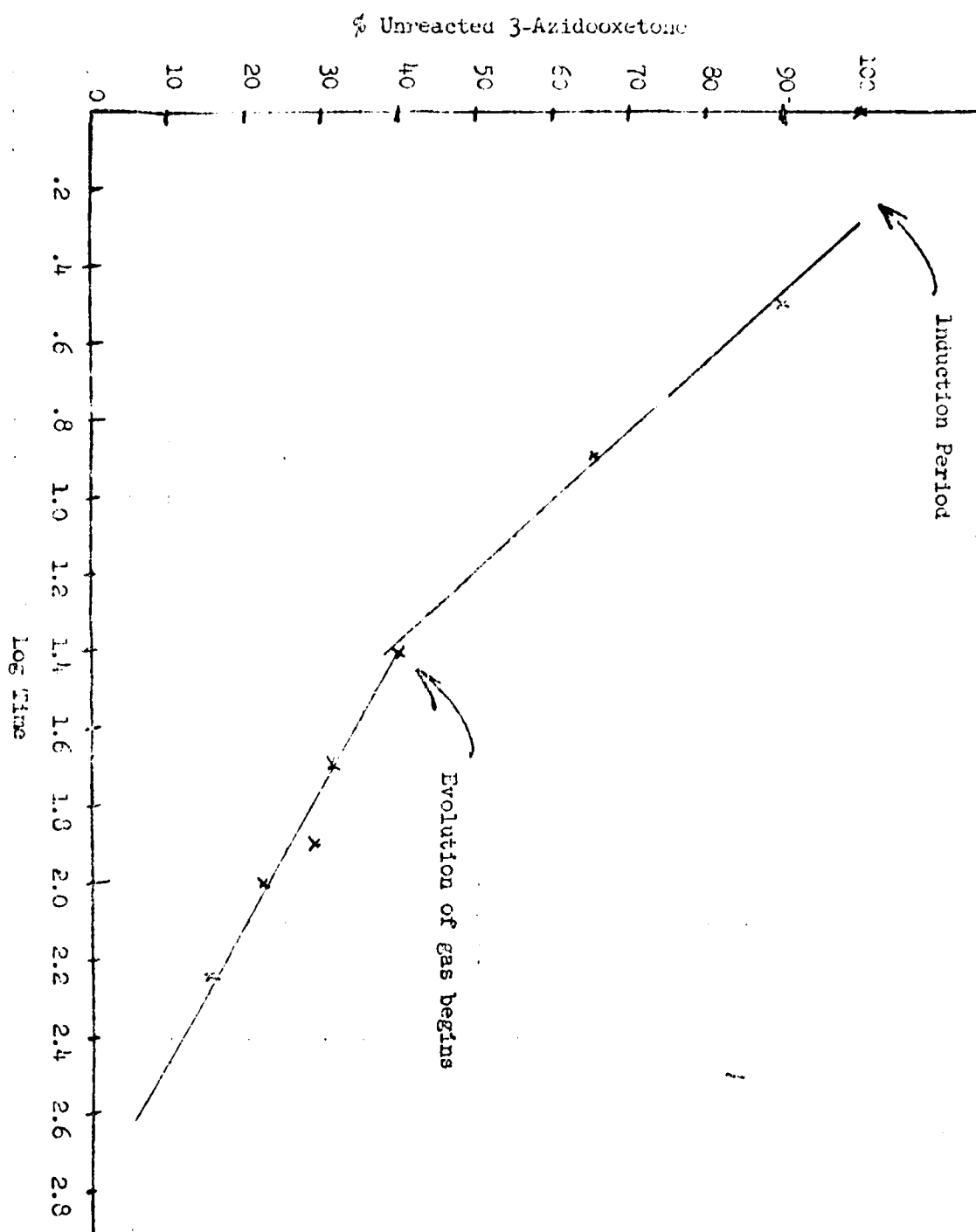
After a number of exploratory experiments were carried out, conditions were found that consistently gave polymeric diols with molecular weight of 3,000 to 3,600. The reactions were carried out in methylene chloride solution at ice-bath temperature with 5 mole % of boron trifluoride etherate as the catalyst. The product was purified by washing with sodium carbonate solution to remove the catalyst, and by a precipitation from methylene chloride-hexane. Yields of the purified polymer were generally 50-65%. The polymerization was scaled up to

the 150 g level to give a product with a molecular weight of 3110. Hydroxyl functionality of the material, determined by the silylation method was 2.0, and the density was 1.336.

The difunctional nature of the polymer was confirmed by converting it to a linear polyurethane. The polymer was treated with a stoichiometric amount of 2, 4-tolylenediisocyanate in methylene chloride with ferric acetylacetonate as catalyst, and removal of solvent gave a rubbery polymer. A sample of the diol was sent to Dr. R. Reed and M. Chan (Naval Weapons Center), who have carried out extensive formulation studies and testing.

Some further studies were made of effects of reaction variables on the polymerization of 3-azidooxetane with the objective of facilitating the preparation of multi-pound quantities. The above conditions result in incomplete conversion of the monomer, and recovery of monomer is a tedious step. Higher catalyst levels were investigated to alleviate this problem. Under parallel conditions, 5 mole% of catalyst gave a 50-60% yield with a molecular weight of 3,000; 10 mole % gave a 50% yield of 2400 molecular weight product; 15 mole% gave an 80% yield of insoluble rubber.

In one experiment, (Fig 1) the rate of disappearance of 3-azidooxetane was followed by glc. A break in rate was observed at 60% reaction, corresponding with the yield of isolated polymer under these conditions. At this point, slow evolution of gas was observed. The nature of this secondary reaction is unknown.



Polymerization of 3-Azidooxetone by $\text{BF}_3 \cdot \text{Et}_2\text{O}$
Figure 1

Mixtures of methylene chloride and hexane gave results similar to those using methylene chloride as the reaction solvent. Ether, however, gave only a low conversion to low molecular weight polymer.

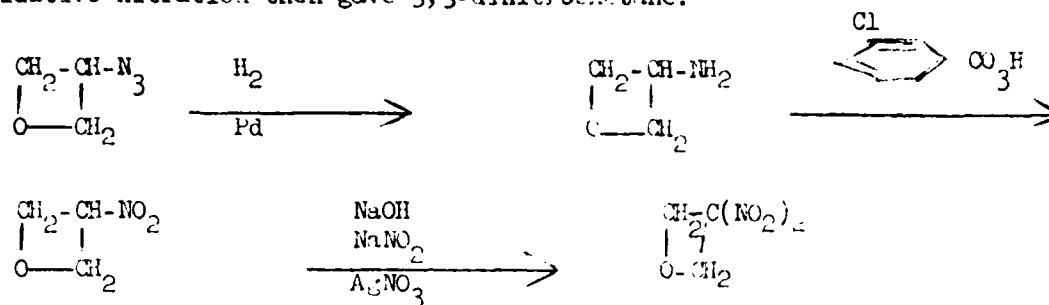
The properties and solubilities of the polymers were a function of the molecular weights, as shown below. For ease of formulation, it may be desirable to aim for molecular weights lower than our original goal of approximately 3,500.

<u>Molecular Weight</u>	<u>Physical State</u>	<u>Solubility</u>		
		<u>Methylene Chloride</u>	<u>Hexane</u>	<u>Acetate</u>
<1200	liquid	+	+	+
1200-1800	fluid oil	+	+-	-
1800-2800	viscous oil	+	-	+
2800-3400	gum	-	-	+
3400	rubber	-	-	-

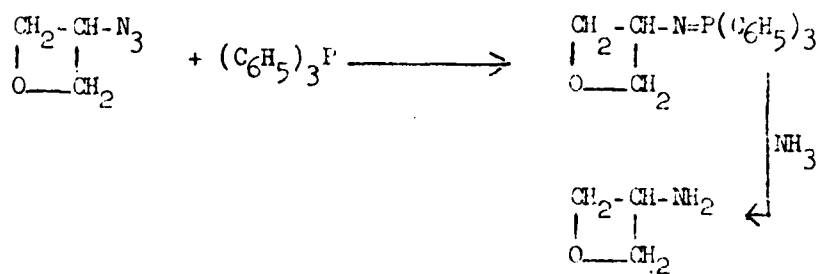
Work at SKI² showed that control of molecular weight could be achieved with several oxetanes by using butanediol complexed with two equivalents of boron trifluoride etherate as the initiator. We intend to apply this procedure to the preparation of larger amounts of the 3-azido-oxetane polymer.

Synthesis of 3,3-Dinitrooxetane. In the previous report,¹ the first synthesis of 3,3-dinitrooxetane was described. Hydrogenation of 3-azido-oxetane, catalyzed by palladium, gave 3-amino-oxetane, which was converted to 3-nitro-oxetane by oxidation with m-chloroperoxybenzoic acid.

Oxidative nitration then gave 3,3-dinitrooxetane.



The hydrogenation 3-azidooxetane was poorly reproducible, apparently because of catalyst poisoning, and large amounts of the catalyst were needed. Alternative reagents that were investigated unsuccessfully are lithium aluminum hydride, sodium borohydride in isopropanol, hydrazine and zinc. Triphenylphosphine, however, proved to be a reliable reducing agent for this reaction. Triphenylphosphine reacted with 3-azidooxetane at room temperature in methylene chloride to give the phosphimine, and 3-aminooxetane was released by the addition of ammonia. The overall yield was nearly quantitative.



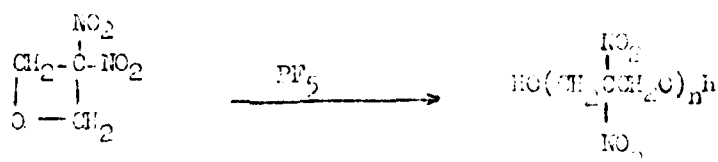
The oxidation of this phosphimine intermediate with *m*-chloroperbenzoic acid directly to 3-nitrooxetane was also studied. The reaction gave 3-nitrooxetane, but the yield was only 20%. No reaction took place when 3-azidooxetane was treated with *m*-chloroperbenzoic acid.

Efforts are in progress to find an alternative oxidizing agent to *m*-chloroperbenzoic acid for the conversion of 3-aminooxetane to

3-nitrooxetane. Reactions with potassium permanganate and chromium trioxide failed. Peracetic acid in refluxing dioxane dichloride gave a 10% yield of 3-nitrooxetane.

Another erratic step in the synthesis of dinitrooxetane was the oxidative nitration, with yields of 0-10%. An improved method was found to be reaction of the acid of nitrooxetane with tetranitromethane providing a 60% yield of dinitrooxetane.

Previously, unsuccessful attempts were made to polymerize 3, 3-dinitrooxetane under the conditions that were used for 3-fluoro-3-nitrooxetane: bubbling phosphorous pentafluoride into a methylene chloride solution of the monomer. Subsequently, an excess of phosphorous pentafluoride was kept in contact with a solution of 3, 3-dinitrooxetane in methylene chloride for 30 hours. Some unchanged monomer was still recovered but the bulk of the material had polymerized. A 62.8% yield of solid polymer with a molecular weight of 2870 was obtained, as well as a 21% yield of lower molecular weight material. The molecular weights were determined by vapor pressure osmometry in acetone. The density of the material was 1.59 and the melting point was $100 \pm 2^\circ\text{C}$.

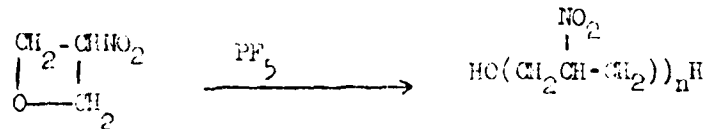


With the objective of obtaining lower melting polymers, the copolymerization of 3,3-dinitrooxetane was examined. Initially, 3-fluoro-3-nitrooxetane was used as the comonomer because it was expected to be similar in reactivity to 3,3-dinitrooxetane. Three preliminary experiments with varying amounts of 3,3-dinitrooxetane (DNO), 3-fluoro-3-nitrooxetane (FNO) and phosphorous pentafluoride are summarized below.

Charge (mmole)			% DNO Recov	Copolymer		
DNO	FNO	PF ₅		Mp	Mol % FNO	MW
1.5	0.5	1	63	147°	33	4260
1.5	0.5	2	59	137°	11	3460
3.3	0.2	1	63	171°	4	-

Of importance is the fact that significant reductions of the melting point were achieved by the incorporation of small amounts of a comonomer that is structurally very similar to 3,3-dinitrooxetane. What is needed is a comonomer with reactivity similar to that of DNO and less similar geometrically to provide polymers with low glass transition temperatures.

It was found that 3-nitrooxetane was also polymerized with phosphorus pentafluoride in methylene chloride. A 90% yield of low molecular weight polymer was obtained (MW 400) with gummy consistency.



Unsuccessful attempts were made to synthesize 3-oxetyl fluorodinitroethyl ether. Reactions of 3-hydroxyoxetane with trifluoromethanesulfonic anhydride gave complex unstable products. Similarly, reactions of 3-hydroxyoxetane with fluorodinitroethyl triflate did not give the desired ether.

B. Experimental

3-Aminooxetane. A solution of 50 g (0.50 mole) of 3-azidoxetane in 800 ml of methylene chloride was cooled with an ice bath and 132.5 g (0.50 mole) of triphenylphosphine was added. The solution was

allowed to stand for 30 minutes at 0-5°C and for 3.5 h at room temperature. The methylene chloride was removed in vacuo to leave an off-white solid. An ice-cold solution of methanol saturated with ammonia was then added and the resulting orange solution was stirred for 40h at 0-5°C. Distillation gave 31.98 g (87.6%) of somewhat impure 3-aminooxetane, bp 50-82°C (60-70mm). A repetition of this reaction gave 29.56 g (81.0%) of 3-aminooxetane. The combined distillation residues were extracted with ether, and distillation gave an additional 8.8 g of 3-aminooxetane. The combined yield for the two reactions was 70.32 g (96.3%) of 3-aminooxetane: ¹H NMR (CDCl₃) δ 2.03 (s, 2 H, -NH₂); 4.0-4.8 (m, 5 H, oxetane); IR (film) 3350 (NH₂), 3000, 2900 (C-H), 1605 (NH₂), 970 cm⁻¹ (oxetane); n_D²⁶ 1.4500.

3-Nitrooxetane. A solution of 7.3 g (0.10 mole) of 3-aminooxetane in 100 ml of 1,2-dichloroethane was added over 1 hr to a refluxing solution of 71 g (0.35 mole) of 85% m-chloroperbenzoic acid in 600 ml of 1,2-dichloroethane. The reaction mixture was heated at reflux for 3-1/4 hrs longer and was then allowed to stand at room temperature overnight. The precipitated m-chlorobenzoic acid was filtered and the filter cake was washed with 70 ml of 1,2-dichloroethane. The 1,2-dichloroethane was removed in vacuo and the solid residue was distilled in a Kugelrohr apparatus to give 6.35 g (61.6%) of somewhat impure 3-nitrooxetane, bp 77°C (0.5-1.0mm). Preparative gc (9% QF-1 on Chromosorb W, 120°C) afforded an analytical sample: ¹H NMR (CDCl₃) δ 4.87 (m, 4 H, -CH₂OCH₂-); 5.23 (m, 1 H, CHNO₂); IR (CH₂Cl₂) 3000, 2940 (CH); 1550, 1370 (NO₂); 980 cm⁻¹ (oxetane); n_D²⁰ 1.4618; d=1.33.

Anal. Calcd for C₃H₅NO₃: C, 34.96; H, 4.89. Found: C, 34.77; H, 4.87.

Reaction of 3-Aminooxetane with Peracetic Acid. To a refluxing solution of 30 ml of dichloroethane and 40 g of 40% peracetic acid in acetic acid was added dropwise a solution of 5.0g(0.68 mole) of 3-aminooxetane in 20 ml of dichloroethane. An exothermic reaction occurred with slow green color formation over one hour. The solution was refluxed for 4 hours and allowed to stand overnight. The solution was washed with a 1:1 ammonium hydroxide-water solution, separated and the solvent evaporated to yield 1.2 g of 3-nitrooxetane (17%) by nmr assay.

3,3-Dinitrooxetane by Oxidative Nitration. A cold solution of 3.385 g (.033 mole) of 3-nitrooxetane, 1.45 g (0.36 mole) of sodium hydroxide and 2.56 g (.036 mole) of sodium nitrite in 72 ml of water was added to a stirred solution of 12.2 g (.072 mole) of silver nitrate in 25 ml of water at 0-5°C. An immediate black suspension formed. After the reaction mixture was stirred at 0-5°C for two h, 25 ml of a saturated sodium chloride solution was added and stirring was continued for 30 min. The reaction mixture was then filtered through celite and the filter cake was washed with 10 ml of water and with 100 ml of ether. The aqueous solution was extracted with this 100 ml ether and with two more 100 ml portions of ether. The combined ether solutions were dried and solvent was removed in vacuo to leave 1.61 g of crude product. Column chromatography (silica gel, methylene chloride-hexane) gave 1.07 g (21.9%) of pure 3,3-dinitrooxetane: mp 70-71°C; ^1H NMR (CDCl_3) δ 5.27 (s); IR (CH_2Cl_2) 3000, 2940 (CH), 1580, 1325 (NO_2), 1000 cm^{-1} (oxetane); $d=1.55$.

Anal. Calcd for $\text{C}_3\text{H}_4\text{N}_2\text{O}_5$: C, 24.34; H, 2.72. Found: C, 24.54; H, 2.80.

3,3-Dinitrooxetane from Tetranitromethane. A solution of 1.03g (0.010 mole) of 3-nitrooxetane and 2.0 g (0.010 mole) of tetranitromethane in 5 ml of methanol was added dropwise, with stirring over a 20 min period, to a solution of 0.42 g (0.010 mole) of sodium hydroxide in 1 ml of water and 2 ml of methanol at 0°C. Stirring was continued for 30 min and 10 ml of water was then added. The pH was adjusted to 9-10 with sodium hydroxide, and the mixture was extracted with ether (3 x 25 ml). The combined ether solutions were washed with water and dried. Removal of solvent gave 0.89 g (60%) of 3,3-dinitrooxetane.

Polymerization of 3,3-Dinitrooxetane. A dry 100 ml flask, fitted with a syringe valve, was loaded with a solution of 0.113 g (0.76 mmol) of 3,3-dinitrooxetane in 0.5 ml dry methylene chloride, and was flushed with nitrogen. After 40 ml of nitrogen was removed by syringe, 40 ml of (1.6 mmol) phosphorus pentafluoride was added. After 30 h. solvent and catalyst were removed under vacuum and the remaining white solid was extracted with 15 ml of methylene chloride. Removal of solvent in vacuo left 0.018 g (15.9%) of 3,3-dinitrooxetane.

The solid insoluble in methylene chloride was extracted with 15 ml of ethyl acetate. Removal of solvent in vacuo left 0.024 g (21.2%) of a white solid: MW (VPO, ethyl acetate) 484; IR (acetone) 3550 (OH); 1575, 1320 cm^{-1} (NO_2). The solid remaining after extraction with ethyl acetate was taken up in acetone and solvent was then removed in vacuo to give 0.071 g (62.8%) of poly (3,3-dinitrodimethylene ether) as a white solid: mp 200-202°C; ^1H NMR (acetone- d_6) δ 4.67 (br s); IR (acetone) 3600 (OH); 1565, 1320 cm^{-1} (NO_2); MW (VPO, acetone) 2870; $d=1.59$ (perfluoro-2-

butyltetrahydrofuran-hexane).

Copolymer of 3,3-Dinitrooxetane and 3-Fluoro-3-nitro-oxetane. Phosphorus pentafluoride (25 ml, 1 mmol) was added to a solution of 0.222g (1.5 mmol) of 3,3-dinitrooxetane and 0.069 g (0.5 mmol) of 3-fluoro-3-nitrooxetane in 1.5 ml of methylene chloride at 0°C as in the above example. A precipitate formed immediately. The mixture was stirred at 0-5°C for 5 h and 10 ml of methylene chloride was added. The precipitate was filtered and was washed with 5 ml of methylene chloride. Removal of the methylene chloride gave 0.14 g (63%) of recovered 3,3-dinitrooxetane. The precipitate was dissolved in ethyl acetate, washed with water, dried and stripped of solvent to give 0.064 g of copolymer, mp 147°C (no darkening to 245°C); MW (VPO, EtOAc) 4260; ^{19}F NMR (Acetone) δ 142.8 (m). Quantitative NMR, using a known amount of benzotrifluoride as reference, showed that the material contained 33 mole % of 3-fluoro-3-nitrooxetane units.

When this reaction was repeated using 2 mmoles of phosphorus pentafluoride with a reaction period of 20 h, 0.13 g (59%) of the 3,3-dinitrooxetane was recovered and 0.064 g of copolymer was obtained: mp 137°C; MW (VPO, EtOAc) 3460; ^{19}F NMR (acetone) δ 124.8; 11 mole % 3-fluoro-3-nitrooxetane units by NMR.

The reaction was repeated using 0.562 g (3.8 mmol) of 3,3-dinitrooxetane, 0.025g (0.2 mmol) of 3-fluoro-3-nitrooxetane, and 1 mmol of phosphorus pentafluoride, with a reaction period of 42 h at room temperature. Under these conditions 0.354 (63%) of the 3,3-dinitrooxetane was recovered and 0.053 g of copolymer was obtained, mp 171°C; ^{19}F NMR

(acetone) ϕ 143.0; 4 mole % 3-fluoro-3-nitrooxetane units.

Polymerization of 3-Azidooxetane. Freshly distilled boron trifluoride etherate (11 g, 0.077 mole) was added with stirring to a solution of 150 g (1.5 mole) of 3-azidooxetane in 750 ml of dry methylene chloride with ice-bath cooling. The reaction temperature rose from 5°C to 20°C in 10 min and returned to 5°C in 90 min. After 3.5 h, 300 ml of methylene chloride was added and the reaction was quenched by the addition of 45 ml of cold 2M potassium carbonate solution. The mixture was stirred for 30 min and the solution was then dried over magnesium sulfate. The methylene chloride solution was added to 1100 ml of hexane. The mixture was stirred for 30 min and was allowed to stand for 2.5 h. The precipitate was washed with hexane (2 x 300 ml) and dried under vacuum to give 82.2 g (55.2%) of a tacky resin: molecular weight 3110 (vapor osmometer, ethyl acetate); hydroxyl functionability 2.0; density 1.336; ^1H NMR (CDCl_3) δ 3.58 (s); IR (CH_2Cl_2) 3,000, 2,900 (CH), 2150 (N_3), 1135 cm^{-1} (C-O-C).

Removal of solvent from the methylene chloride-hexane solution left 33.7 g of an equal mixture of oligomers and 3-azidooxetane, as determined by NMR.

Another run using 50g (0.5 mole) of 3-azidooxetane and 3.6g (0.025 mole) of boron trifluoride etherate gave 32g (64%) of fractionated polymer, MW 3610; hydroxyl functionality 2.0.

Gumstock Preparation. A solution of 2.158 g (0.705 mmol) of 3-azidooxetane polymer (MW 3060) and a catalytic amount of ferric acetylacetonate in 2.3g of methylene chloride was flushed with nitrogen, and 0.123g (0.705 mmol) of tolylene-2, 4-diisocyanate was added. A rubbery

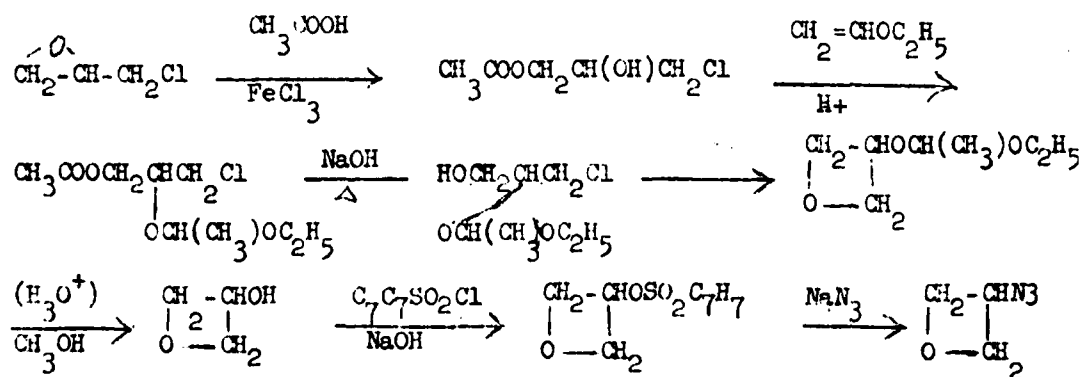
mass formed within 5 min. After 5 days, removal of solvent left a resilient rubber.

III Process Development and Production of 3-Azidooxetane

A. Discussion

The polymerization of 3-azidooxetane has given potentially useful difunctional oligomers. For the evaluation of these materials in formulations, multi-pound quantities are needed. To facilitate the production of such quantities of material, attention was paid to simplifying the reaction procedures and overcoming problems, such as exotherms, that are not apparent in small scale experiments.

A new route to 3-hydroxyoxetane from epichlorohydrin was developed previously on this program¹ using blocking agents to control the direction of ring closure. Acetic acid was added to epichlorohydrin and the resulting secondary alcohol was protected as a base-resistant acetal group. Base hydrolysis of the acetate group and ring closure gave the blocked oxetane, which was deblocked with mild acid. Conversion of 3-hydroxyoxetane to the tosylate followed by displacement with sodium azide gave 3-azidooxetane.

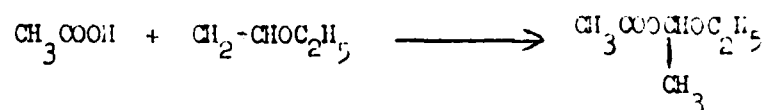


Changes made in each of these steps to facilitate scale-up are described below.

Epichlorohydrin-Acetic Acid Reaction. The most significant changes in the first step of the sequence were minimizing the amounts of excess acetic acid and of ferric chloride catalyst to allow the use of the crude product in the next step without further processing. The reaction time was reduced from 2 days to several hours by using a reaction temperature of 75-85°C instead of 0-10°C. The reaction is highly exothermic, but the temperature can be controlled by means of a water bath. Scale-up to the 150 mole level was accomplished using a 22 liter reaction flask.

3-Chloro-2-(1-ethoxyethoxy)-1-propyl acetate. In our previous laboratory procedure, 3-chloro-2-hydroxy-1-propyl acetate was treated with ethyl vinyl ether in methylene chloride using 10% of pyridinium p-toluenesulfonate as the catalyst. In the scale-up study, the more effective catalyst, p-toluenesulfonic acid hydrate, was used and the solvent was omitted. Thus, crude 3-chloro-2-hydroxy-1-propyl acetate containing dissolved ferric chloride from the previous step was treated with a 10% excess of ethyl vinyl ether and 1% of the catalyst. The reaction was exothermic, and the catalyst slowly lost its effectiveness in the mixture. These problems were solved by the incremental addition of both the vinyl ether and catalyst to the alcohol. The reaction product was simply washed with water and the wet material was used in the subsequent step.

The yield of blocked material, established by distilling an aliquot amounted to ca 75%. A side reaction product was identified as the acetic acid-ethyl vinyl ether adduct (5-10%).



Some low-boiling material (10%) and a viscous distillation residue appeared to contain ethyl vinyl ether polymers.

3-Chloro-2-(1-ethoxyethoxy)propanol and 3-(1-Ethoxyethoxy)-oxetane. In the laboratory scale synthesis of 3-(1-ethoxyethoxy)oxetane a suspension of 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate was heated at reflux with an excess of aqueous sodium hydroxide. In larger scale reactions, the heat liberated by the ester hydrolysis was found to be significant, but the reaction was readily controlled by gradually adding the acetate to the hot alkali with cooling. The cyclization of the resulting propanol derivative to 3-(1-ethoxyethoxy)oxetane was then accomplished by heating the two-phase mixture with vigorous stirring at 108-115° for 4-5 hrs. The product, at this stage, contained considerable amounts of nonvolatile by-products, and the material was purified by vacuum distillation. In an average 150 mole run, only 8 to 8.5 kg of distilled material of estimated 30% purity was obtained, corresponding to 30-40% yield based on epichlorohydrin used in the first step. The reasons for the low yields of 3-(1-ethoxyethoxy)oxetane have not been determined, but contact of the aqueous and organic phases may be inadequate. More efficient stirring or the use of phase transfer catalysts would be beneficial.

3-Hydroxyoxetane. Removal of the acetal blocking group did not present difficulties in scale-up. 3-Hydroxyoxetane was obtained in high yield by treating a methanolic solution of 3-(1-ethoxyethoxy)oxetane from the proceeding step with p-toluenesulfonic acid hydrate. The reaction was only mildly exothermic and was completed in several hours at 30-35°C. Removal of volatiles gave material of 75-80% purity, that was used without

further purification in the synthesis of 3-oxetyl tosylate.

3-Oxetyl Tosylate. 3-oxetyl tosylate was obtained by reacting 3-hydroxyoxetane with p-toluenesulfonyl chloride. The process was simplified by using aqueous sodium hydroxide to remove HCl rather than the organic bases that were used previously. Pure crystalline 3-oxetyl tosylate was obtained from relatively impure 3-hydroxyoxetane, and the only work-up needed was air drying.

3-Azidooxetane. In the earlier laboratory procedure, 3-azidooxetane was obtained in 55% yield by heating 3-oxetyl tosylate with sodium azide at 160°C in triethylene glycol. The product was removed by vacuum distillation as it was formed. Yields in 0.4 mole runs were improved to 86-90%. The reaction temperature was lowered to 125-150°C, and the amount of solvent was reduced. The product was generally pure without further purification. In several cases, prolonging the vacuum transfer resulted in contamination of the product with small amounts of triethylene glycol. This contaminant was removed conveniently by treating the material with calcium chloride.

Large scale synthesis of this potentially explosive monomer requires shielding, and preferably, keeping a diluent in the receiver. The solvent volatility problem was eliminated by using polyethylene glycol 400 in place of triethylene glycol. The receiver was loaded with methylene chloride and was kept at -78°C to prevent evaporation of this solvent. The receiver was stirred magnetically to prevent crystallization of the product. The sodium tosylate formed by the displacement reaction is somewhat

less soluble in IEG 400 than in triethylene glycol, and toward the end of the reaction a fluffy precipitate prevented continuation of the distillation. As a consequence, yields were reduced to 66%. After one run, the cooled reaction mixture was filtered and the precipitate was washed with methylene chloride. Continued distillation then increased the yield to 81%.

Approximately 20 lbs of 3-azidooxetane was produced. In addition, 45 lbs of 3-oxetyl tosylate is on hand.

Other Intermediates. Acetic acid, a weak acid with pK 4.76, does not react with epichlorohydrin in the absence of a catalyst. It was found that chloroacetic acid (pK 2.85) and dichloroacetic acid (pK 1.30) gave adducts with epichlorohydrin without a catalyst. These adducts reacted normally with ethyl vinyl ether. In the ring closure step, however, the haloacetate moieties underwent side reactions that consumed base. At this point, problems associated with the acetic acid route were resolved and work with the chloroacetates was discontinued.

B. Experimental

3-Chloro-2-Hydroxy-1-Propyl Acetate. A 22L three-necked flask, fitted with a mechanical stirrer and a reflux condenser with a drying tube was loaded with 9.16 kg (152.54 moles) of glacial acetic acid and 85 g of anhydrous ferric chloride. Epichlorohydrin (13.9 kg, 150.27 mole) was added to the stirred mixture in a slow stream by means of an addition funnel. The reaction temperature increased to $42^{\circ}C$ as 10% of the epichlorohydrin was added in 20 min, and then began to decrease. The remaining epichlorohydrin was added in 5 min and the mixture was heated carefully to $68-70^{\circ}C$. The exothermic reaction resumed and the reaction

temperature was maintained at 70-72°C for 2 h with a 40°C water bath, and then was kept at 83-85°C for 1 h. The product was allowed to cool to ambient temperature overnight, and was used without purification in the subsequent step. Careful temperature regulation is needed to maintain control of the reaction exotherm.

3-Chloro-2-(1-ethoxyethoxy)-1-propyl Acetate. The above crude mixture was placed in a mechanically stirred 50 L flask fitted with a reflux condenser. The flask was cooled with an ice-water bath while 6 kg (83.2 moles) of ethyl vinyl ether was added. *p*-Toluenesulfonic acid hydrate (20 g) was added and the reaction temperature rose to 64-67°C in 7-10 min. When the mixture cooled to 18-20°C, another 6 kg (83.2 moles) of ethyl vinyl ether and then 25 g of the catalyst were added. The reaction temperature rose to 55°C in 15 min. The coolant was removed and the mixture was allowed to cool to ambient temperature in 2 h. The mixture was washed with 25L of water, and the product 31.5 kg (94% yield) was used without purification in the next step. The NMR spectrum showed no major impurities.

3-(1-Ethoxyethoxy)oxetane. A mechanically stirred 50L flask with a reflux condenser was charged with 9L of water and 7.0 kg (175 moles) of sodium hydroxide. The above 3-chloro-2-(1-ethoxyethoxy)-1-propyl acetate was added from an addition funnel over a 3-4 h period while the reaction temperature was maintained at 95-100°C with water-bath cooling. The mixture was allowed to stand overnight and was washed with 5 L of water. The product was stirred with 7 kg of sodium hydroxide and 9 L of water and the mixture was heated at reflux (105-115°C) for 4 h. The product was allowed to cool overnight and the phases were separated. The aqueous phase

was diluted with 4L of water and extracted with 4L of methylene chloride. Distillation of the combined organic phases gave 9.0 kg of product, bp 45-75°C (0.1 mm) shown by NMR to contain 80-85% 3-(1-ethoxyethoxy) oxetane. (33-36% yield based on epichlorohydrin).

3-Hydroxyoxetane. The combined product of two runs by the above procedure was stirred with a solution of 50g of p-toluenesulfonic acid hydrate in 7L of methanol. The reaction temperature rose to 33°C in 20 min and remained at that temperature for 2h. The mixture was allowed to stand overnight. Volatiles were removed at 25-50°C (40 to 0.3 mm) to give 11.6 kg of 70-75% pure (by NMR) 3-hydroxyoxetane.

3-Oxetyl Tosylate. To a stirred suspension of 10.5 kg of p-toluenesulfanyl chloride in 9L of 0.5% sodium hydroxide in a 50L round-bottom flask was added 4.8 kg of crude 3-hydroxyoxetane. The flask was cooled with a water bath, and a solution of 3.9 kg of sodium hydroxide in 4.3L of water was then added, at a rate to maintain a reaction temperature of 70°C. After the addition was complete (75 min), the mixture was stirred at 65-70°C for 45 min. The product was filtered at room temperature and was washed with 3-4L portions of water at 60°C. The white crystalline product was air dried to give 6.3 kg of 98-100% pure oxetyl tosylate (NMR), 23% yield based on epichlorohydrin.

3-Azidooxetane. A mixture of 552 g (2.42 moles) of 3-oxetyl tosylate, 240 g (3.69 mole) of sodium azide and 1030 ml of triethylene glycol was placed in a 5 L round bottom flask equipped with a magnetic stirrer and a vacuum distillation head. The distillation receiver was cooled with

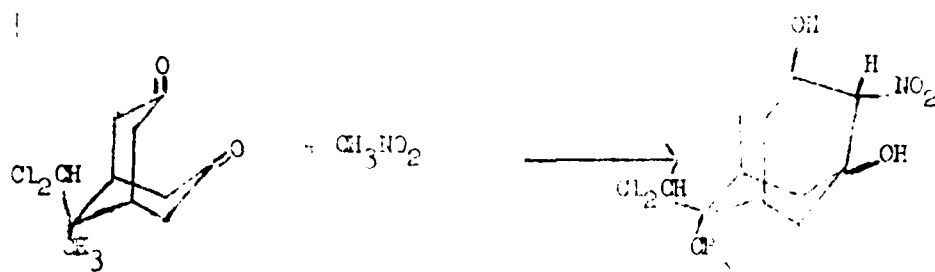
an ice bath. The reaction mixture was heated behind safety shielding, over a 45 min period, to 125-130°C (3-5 mm). Distillation of 3-azidooxetane began at 90°C and the reaction was completed after 2 h at 125-130°C. The distillate was diluted remotely with 100 ml of methylene chloride, and NMR analysis of the product showed 191 g (80% yield) of 3-azidooxetane.

The reaction was scaled up by a factor of 4 using a 22 L flask with a mechanical stirrer. Polyethylene glycol 400 was used as the solvent instead of triethylene glycol. The receiver, stirred magnetically, was loaded before the reaction with 2 L of methylene chloride and was cooled with dry ice. The original distillate, as in the above example, consisted of 660 g of 3-azidooxetane. The polyethylene glycol solution, containing precipitated sodium tosylate, was cooled and filtered. The precipitate was washed with 3-1 L portions of methylene chloride. Distillation of the combined filtrate and washings in the above apparatus gave an additional 150 g of 3-azidooxetane (82% total yield).

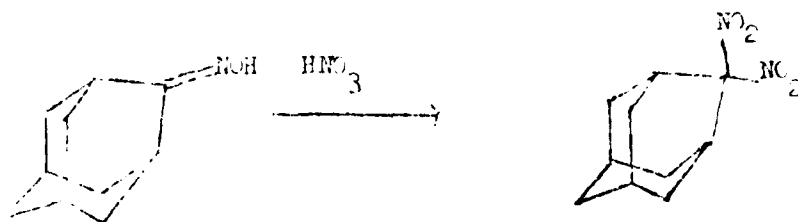
IV Polycyclic Nitro Compounds

A. Discussion

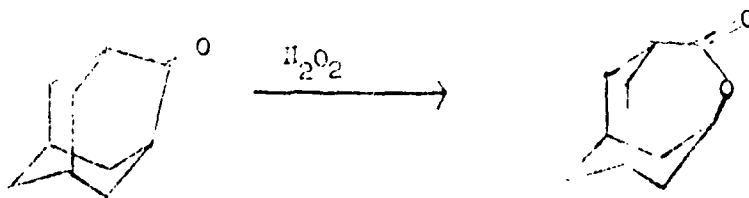
Adamantanes and related structures with nitro substituents comprise a little studied class of compounds, with the potential of providing high density and energy. The bridgehead nitro compounds, 1-nitroadamantane³ and 1,3-dinitroadamantane⁴, have been known for two decades, and recently, 1,3,5,7-tetranitroadamantane has been reported⁵. The only example in the literature with a nitro on the bridge was obtained by the condensation of nitromethane with a bicyclic diketone⁶.



The synthesis of 2, 2-dinitroadamantane by the nitration of adamantanone oxime was recently described at a technical meeting.⁷

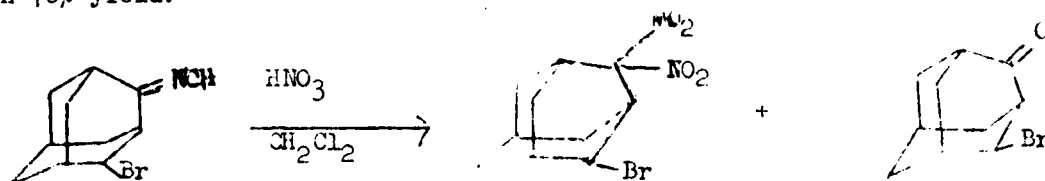


One of our objectives was to extend this reaction to poly-functional substrates, so attempts were made to optimize the preparation of 2,2-dinitroadamantane. Steroid oximes react with nitric acid at low temperatures to give highly colored nitro-nitroso intermediates, which are oxidized to dinitro compounds by the addition of hydrogen peroxide.⁸ Our attempts to nitrate adamantanone oxime at low temperatures with varying concentration of nitric acid or dinitrogen tetroxide gave only trace yields of the dinitro compound. The free ketone was recovered, and when hydrogen peroxide was used, the major product was the lactone resulting from a Baeyer-Villiger rearrangement.



Under Gilbert's⁵ nitration conditions, using refluxing methylen chloride as the reaction medium, we obtained a 30% yield of 2,2-dinitroadamantane. No hydrogen peroxide was needed to oxidize the transient nitro-nitroso intermediate to the dinitro compound, and the latter was even converted to the Baeyer-Villiger product.

Under the same conditions, 4-bromo-2-oximinoadamantane was converted to 4-bromo-2,2-dinitroadamantane in 50% yield. The crude reaction mixture was treated with hydroxylamine to reconvert the by-product ketone to the oxime, and renitration gave the dinitro adamantane in 70% yield.

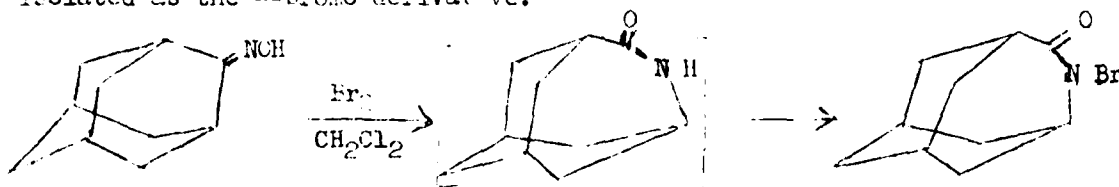


These nitration conditions were applied to 2,6-dioximinoadamantane with the objective of preparing the tetranitro adamantane. The initial attempt to carry out this reaction gave a sharp-melting solid product, but elemental analysis showed that the material is an isomer of the nitro-nitroso compound.

Another approach to introducing nitro groups into steroids is to halogenate an oxime, oxidize the resulting halo nitroso compound, and remove the halogen reductively⁸. This approach was extended to the adamantane system. The reaction of 2-oximinoadamantane with N-bromosuccinimide was found to proceed in high yield to give directly 2-bromo-2-nitroadamantane. As in the direct nitration of the oxime the nitroso intermediate exhibited only transitory existence. It was also observed that the usual peroxide addition step effectively destroys the product.

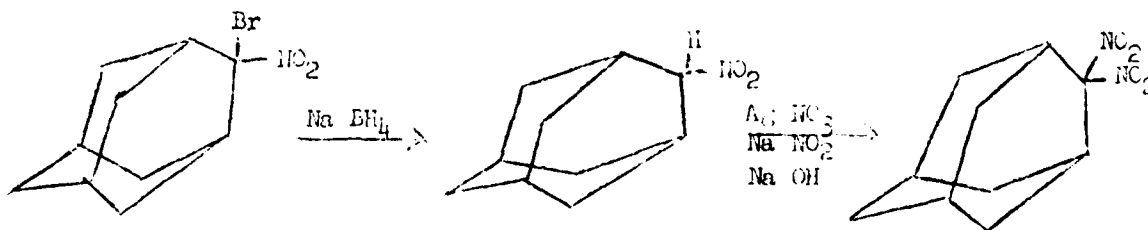
Similarly, the reaction of this oxime with aqueous sodium hypochlorite in ethanol gave 2-chloro-2-nitroadamantane, with only transitory formation of the blue nitroso intermediate.

The presence of water in these reaction was found to be important and the direct reaction of the 2-oximinoadamantane with bromine in methylene chloride gave the expected ring expanded amide, 4-azo-5-homoadamantanone which was isolated as the N-bromo derivative.

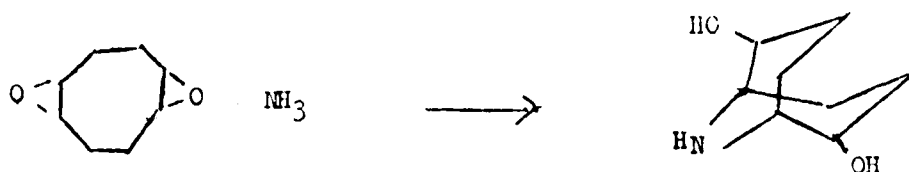


The isolated 4-bromo-4-azo-5-homoadamantanone was unstable, losing bromine on recrystallization.

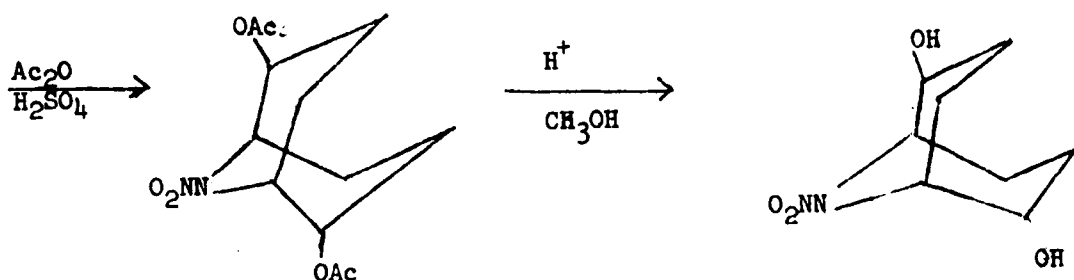
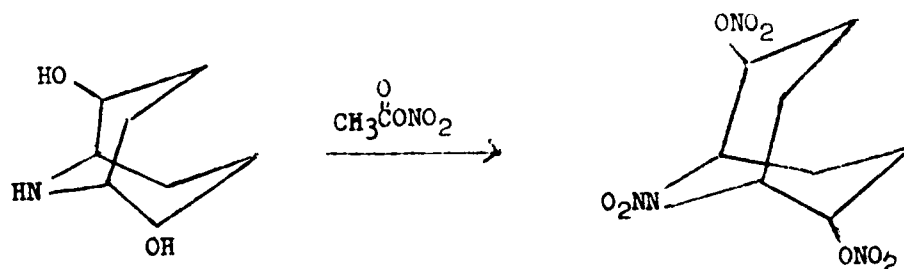
In the steroid work, the 2-bromonitro compounds, but not the 2-chloronitro compounds, were dehalogenated with sodium borohydride.⁸ The adamantane derivatives behaved similarly. Thus 2-bromo-2-nitroadamantane gave good yields of the expected 2-nitroadamantane, but 2-chloro-2-nitroadamantane failed to react under similar conditions. The oxidative nitration of 2-nitroadamantane proceeded normally, and this procedure gave a good overall yield of 2,2-dinitroadamantane.



H. Stetter⁹ discovered the reaction of 1,2,5,6-diepoxyoctane with ammonia to yield 2,6-dihydroxy-9-azabicyclo(3.3.1)nonane.



We have initiated work to convert this bicyclic amine to energetic compounds containing nitramino, nitrate and/or gem-dinitro groups. Nitration with acetyl nitrate in acetic anhydride yielded the nitroamine dinitrate, an impact sensitive solid. Under milder conditions the N-acetyl dinitrate was formed. Transesterification of the nitramine to the diacetate, 2,6-diacetoxy-9-nitro-9-azabicyclo (3.3.1)nonane in high yield was effected by sulfuric acid in acetic anhydride. The diacetate was hydrolyzed in either methanolic potassium hydroxide or methanolic aqueous hydrochloric acid to give 2,6-dihydroxy-9-nitro-9-azabicyclo(3.3.1)nonane.



B. Experimental

2-Bromo-2-nitroadamantane. 4-Bromosuccinimide (12.0 g, 0.067 mole) was added at 20°C to a solution of 4.0 g (0.024 mole) of 2-oximinoadamantane¹⁰ in 100 ml of 50% dioxane-water, and 6 g of solid sodium bicarbonate was added. A light blue color formed that faded over a 1 h period. Solvent was removed under vacuum and the residue was extracted with ether (2X30 ml) to yield a crude solid which when recrystallized from ethanol-water gave 5.0 g (80%) of 2-bromo-2-nitroadamantane, mp 190-191° (sealed tube, sublimes). IR(KBr) 3000, 2900, 1540, 1445, 1340: NMR (CDCl₃) δ 2.9 (2 H), 2.2-1.9 (12 H).

Anal. Calcd for C₁₀H₁₄BrNO₂: C, 46.15; H, 5.38; N, 5.38. Found: C, 46.00; H, 5.30; N, 5.27.

2-Chloro-2-nitroadamantane. Aqueous 5% sodium hypochlorite solution (30 ml) was added to a solution of 0.2 g (0.0012 mole) of 2-oximinoadamantane and 0.2 g of sodium bicarbonate in 20 ml of dioxane. There was an exothermic reaction. The solution was stirred for one hour and 100 ml of water was added. The solid which formed was filtered and recrystallized from ethanol-water to yield 0.2 g (76%) of 2-chloro-2-nitroadamantane, mp 200-201°C (sealed tube, sublimes). IR (KBr) 2960, 2900, 1550, 1455, 1350, 1330.

Anal. Calc'd for C₁₀H₁₄ClNO₂: C, 55.68; H, 6.49; N, 6.49. Found: C, 55.29; H, 6.59; N, 6.30.

2-Nitroadamantane. To a solution of 4.0 g (0.015 mole) of 2-bromo-2-nitroadamantane in 50 ml ethanol and 10 ml of water was added 2.0 g of sodium borohydride and the mixture was stirred for 1 h. GLC

analysis showed that the starting material was consumed. The solution was neutralized with 50% acetic acid solution and the ethanol was evaporated; 50 ml of water was added and the solid which formed was filtered to yield 2.4 g (89%) of 2-nitroadamantane as a waxy solid, mp 165-166°C (subl); IR (KBr): 2950, 2900, 1540, 1450, 1360; nmr: δ 4.25 (t, 1 H), 2.75 (2 H), 1.9-2.1 (12 H).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.29; H, 8.28; N, 7.34.

Found C, 64.83; H, 8.24; N, 7.58.

2,2-Dinitroadamantane. To a solution of 2-nitroadamantane (0.2 g, 0.001 mole) dissolved in 10 ml ethanol was added a solution of 0.4 g of sodium nitrite and 0.2 g of sodium hydroxide in 10 ml of water. This solution was stirred for 10 minutes and 10 ml of water containing 0.5 g of silver nitrate was added. An immediate black precipitate of metallic silver was observed. After 30 minutes of stirring, the solution was mixed with 60 ml of ether and filtered. The ether layer was separated and evaporated to yield 0.2 g (31%) of the crude product, which was found by glc analysis to contain only a small amount of 2-adamantanone. Recrystallization from hexane gave pure 2,2-dinitroadamantane; mp 212-213°C (d, sealed tube); IR: 3150, 3000, 1570, 1460, 1360, 1320; nmr ($CHCl_3$) δ 1.9-2.1 (12 H), 3.4 (2 H); density 1.40.

Anal. calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.19; N, 12.38.

Found: C, 53.30; H, 6.16; N, 12.25.

Direct Nitration of 2-Oximinoadamantane. To a solution of 0.10 g (0.0006 mole) of 2-oximinoadamantane in 10 ml of refluxing

methylene chloride was added dropwise 2 ml of 10-100% nitric acid. A light bluish color formed and after several minutes dissipated. Glc analysis after 30 minutes showed two peaks representing about 70% 2-adamantanone and 30% 2,2-dinitroadamantane. The solvent was evaporated and the residue was washed with 20 ml of water, redissolved in 10 ml of methylene chloride and chromatographed on a medium pressure silica gel column with methylene chloride. The material which passed rapidly thru the column was isolated from the methylene chloride solution by evaporation to yield 30 mg (21%) of 2,2-dinitroadamantane identical with the material prepared above. The column destroyed the ketone and no other materials were recovered from the column. Repetition of this procedure using refluxing chloroform in place of methylene chloride yielded only 2-adamantanone with no 2,2-dinitroadamantane detected by glc.

4-Bromo-2,2-dinitroadamantane. 4-Bromo-2-adamantanone¹¹, mp 161-163°C, was converted to its oxime, mp 175-176°C. To a solution of 1.0 g (0.0044 mole) of the oxime in 50 ml of refluxing methylene chloride was added dropwise 5 ml of 10-100% nitric acid. There was an immediate green color formed which disappeared in about 1 minute. The solution was refluxed for 20 min, cooled, and washed with 20 ml of 10% sodium carbonate solution. The methylene chloride was evaporated to yield a waxy solid. The infrared spectrum of the crude material showed approximately a 50-50 mixture of 4-bromo-2-adamantanone and 4-bromo-1,2-dinitroadamantane (1720 and 1590 cm⁻¹). The crude solid was dissolved in 20 ml of ethanol and 1 g of hydroxylamine hydrochloride and 5 ml of 10% sodium carbonate solution were added. This solution was refluxed one hour and allowed to stand 10

hours at room temperature. The ethanol was evaporated and the organic materials were extracted with methylene chloride. This solution was heated to reflux and 2 ml of 90-100% nitric acid was added. A green color again formed and disappeared. After 30 min, the solution was cooled, washed with 10 ml of 10% sodium carbonate solution, and the methylene chloride was evaporated. The infrared spectrum of the crude product showed a 30-70 ratio of ketone to dinitro compound. The above procedure for hydroxylation, nitration, and extraction was repeated for a third time. The infrared spectrum of the crude material showed the ketone was essentially consumed. The crude solid was recrystallized from hexane to yield 0.8 g (60%) of 4-bromo-2,2-dinitroadamantane, mp 227-230°; IR: 3050, 3000, 1535, 1450, 1330, 1355, 1315; nmr δ 1.9-2.1 (10 H), 3.2 (1 H), 3.6 (1 H), 4.5 (1 H).

Anal. Calcd for $C_{10}H_{13}BrN_2O_4$: C, 39.36; H, 4.29; N 9.18.
Found: C, 39.04; H, 4.73; N 8.47.

Nitration of 2,6-Dioxiadamantane. 2,6-Admantanedione was prepared according to the literature¹² and was converted to its oxime. To a suspension of 1.0 g (0.0051 mole) of the oxime in 50 ml of methylene chloride was added dropwise a total of 3 ml of 90-100% nitric acid over the course of 20 minutes. The solution became light blue immediately, and when 15 drops of the acid was added, the solid dissolved. After the addition was complete, the solution was refluxed for 20 min during which time oxides of nitrogen were liberated. The solution was cooled and neutralized with 5% potassium hydroxide solution to pH 9. The methylene chloride layer

evaporated to yield 0.8 g of a greenish semi-solid. Half of this solid was chromatographed on a silica gel preparative TLC plate with methylene chloride. Four major bands were extracted from the silica gel with ethanol. The fastest moving band showed IR peaks indicative of a nitroketone and was not further identified (yield approximately 5 mg.). The next fastest band was identified as 2,6-adamantandione (yield 30 mg 20%). A band which did not move on the plate was identified as 2,6-dioximinoadamantane (yield 50 mg, 10%). The remaining band which was the slowest of the bands which moved consisted of 50 mg (10%) of white solid, mp 164-165°C; IR 3090, 3000, 1575, 1440, 1340.

Anal. Calc. for $C_{10}H_{12}N_4O_6$: C, 42.25; H, 4.25; N, 19.71.
Found: C, 42.20; H, 4.32; N, 19.23.

Reaction of 50 mg of the solid in 10 ml of ethanol and 2 ml of 30% hydrogen peroxide at 70 for one hour resulted in loss of the IR nitro absorptions.

Reaction of 2,2-Dinitroadamantane with Hydrogen Peroxide. A solution of 50 mg of 2,2-dinitroadamantane and 5 ml of 30% hydrogen peroxide in 10 ml of ethanol was refluxed for one hour. IR and ^{13}C showed mainly 4-oxo-5-homoadamantane, compared with an authentic sample^{13,12}.

2,6-Dinitrato-9-nitro-9-aza-bicyclo(3.3.1)nonane. To a solution of 100 ml of acetic anhydride and 4.0 g (0.025 mole) of 2,6-dihydroxy-9-azabicyclo(3.3.1)nonane was added 0.5 g of solid sodium chloride and 25 ml of 95% nitric acid. The reaction was exothermic and oxides of nitrogen were released for a 30 min period. The mixture was allowed to stand for 16 h and was then quenched with one liter of water. The solid

which formed was filtered and recrystallized from ethanol-water to yield 3.6 g (51%) of 2,6-dinitroxy-9-nitro-9-azabicyclo(3.3.1)nonane, mp 119-120°C. IR: 3050, 3000, 1620, 1520, 1430, 1310, 1260; nmr: δ 2.05 (8 H), 5.0 (4 H). The material was detonated by a moderate hammer blow.

Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 32.88; H, 4.11; N, 12.13.
Found: C, 35.02; H, 4.50; N, 18.28.

2,6-Dinitrato-9-acetoxy-9-aza-bicyclo(3.3.1)nonane. A mixture of 150 ml of acetic anhydride, 0.1 g sodium chloride and 20 ml of 90-100% nitric acid was stirred for 1 h with cooling. Then 8.0 g (0.5 mole) of 2,6-dihydroxy-9-azabicyclo(3.3.1)nonane dissolved in 50 ml of acetic anhydride was added over 15 min, keeping the temperature below 50°C. The reaction was stirred for one h and was then added to one liter of water. The solid which formed was filtered and recrystallized from ethanol to yield 9.0 g (61%) of 2,6-dinitrato-9-acetoxy-9-azabicyclo(3.3.1)nonane, mp 99-101°C (ethanol); 107-109°C (hexane); IR: 3050, 3000, 1620, 1400, 1310; nmr: δ 2.0 (11 H), 4.8 (4 H).

Anal. Calcd for $C_{10}H_{12}N_2O_7$: C, 41.52; H, 5.19; N, 14.53.
Found: C, 42.08; H, 5.01; N, 14.05.

2,6-Diacetato-9-nitro-9-azabicyclo(3.3.1)nonane. Concentrated sulfuric acid (3 ml) was added dropwise to a solution of 1.0 g (0.0037 mole) of 2,6-dinitroxy-9-nitro-9-azabicyclo(3.3.1)nonane in 30 ml of acetic anhydride at 2°C and the solution was allowed to warm to 20°C. After one hour, the solution was poured into 500 ml of ice and water and the solid which formed was filtered. Recrystallization from ethanol yielded 0.67 g (75%) of 2,6-diacetoxy-9-nitro-9-azabicyclo(3.3.1)nonane, mp 152-153°C; IR: 3050, 1720, 1520, 1420, 1360; nmr: δ 2.05 (14 H), 4.9 (4 H); τ

mp 152 (lit 2340).

Anal. Calcd for $C_{12}H_{11}N_2O_6$: C, 50.70; H, 5.64; N, 9.69.

Found: C, 50.16; H, 6.26; N, 9.84.

2,6-Dihydroxy-9-nitro-9-azabicyclo(3.3.1)nonane. A solution of 3.0 g (0.015 mole) of 2,6-diacetoxy-9-nitro-9-azabicyclo(3.3.1)nonane in 50 ml of methanol and 1 ml of concentrated aqueous hydrochloric acid solution was refluxed for 2 h and the methanol was evaporated. The residue was extracted with 30 ml of water and 50 ml of ether. The ether layer was separated and the product was precipitated from the ether with 30 ml of hexane. The solid thus obtained was recrystallized from ethanol to yield 1.1 g (33%) of 2,6-dihydroxy-9-nitro-9-azabicyclo(3.3.1)nonane, mp 143-145°C; IR: 3400, 3050, 1520, 1430, 1320; nmr δ 2.0 (3H), 4.0 (2 H), 4.8 (2 H).

Anal. Calcd for $C_9H_{11}N_2O_4$: C, 47.52; H, 6.93; N, 13.86.

Found: C, 47.56; H, 7.01; N, 13.97

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